Modeling chemical partitioning at the water-sediment interface

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Background and objective

- A variety of approaches have been developed to predict chemical mass balance between the water column and benthic sediment.
- Some more mechanistic than others. Most utilize some empirically-derived components to account for the many physical, chemical, biological, and temporally varying processes that may affect chemical exchanges between water and sediment.

- Objective is to compare approaches in models commonly used for pesticide registration review.

No judgement. Just observations.
Physical mechanisms related to chemical transport within and across the sediment bed

• Dissolved-phase sorption onto bed sediments
• Sorbed-phase settling with suspended sediments
• Subduction of sorbed material into the bed by bioturbation
• Pore-water diffusion both within sediment and with overlying water layer
• Bulk sediment motion and resuspension from turbulence

These processes are represented more or less, or at least differently, in different models.
Dominant models used for pesticide registration evaluation at the national level

- VVWM – Variable Volume Water Model (USEPA-OPP)
- TOXSWA – TOXic substances in Surface Waters (Wageningen UR)

Others with some historical significance
- EXAMS – Exposure Analysis Modeling System (USEPA-ORD)
- RIVWQ – Chemical transport model for riverine environments (Waterborne Environmental, Inc.)
- AGRO-2014 (Stone Environmental, Inc. / Canadian Environmental Modeling Centre)
Commonalities

Chemical load

Dissolved \text{Sorption} \text{Particulate}

Degradation

Mass transfer

Dissolved \text{Sorption} \text{Particulate}

Degradation
TOXWA - TOXic substances in Surface Waters

- Volatilization
- Sorption
- Degradation
- Advection
- Diffusion

Chemical load:
- Dissolved
- Particulate

Biota

Outflow
RIVWQ - water quality model for riverine systems

Chemical load

Dissolved

Sorption

Volatilization

Degradation

Particulate

Outflow

Diffusion

Direct partitioning

Settling

Resuspension (bed scour or constant rate)

Sorption

Burial

Dissolved

Particulate

Degradation
Direct partitioning with bed sediment

Empirical equation in RIVWQ to calculate the direct partitioning of dissolved residues in the water column from contact with bed sediment:

\[
\frac{dM_{\text{bed}}}{dt} = (K_d \times F_{DW} \times C_W \times V_{bind} \times \rho_b \times SA)
\]

Achieved better match to water and sediment concentrations measured in shallow water field studies.

Conceptualize this as the fraction of the water column in direct contact with bed sediment during a simulation time step.
One aspect of uncertainty

What is the sensitivity around default values:

- PRBEN = 0.5
- Mass transfer coefficient = $1 \times 10^{-8}$ m/day
- Suspended sediment concentration = 30 ppm
- Active sediment zone = 5 cm?

From: Chapra, 1996
Methods & materials

PWC using MS-cotton

• 1 kg/ha application of a stable chemical
• Koc=500 cc/g
• Single rainfall event
• Examine daily average aqueous concentration in water column and benthic zone
• Modify default properties one-by-one
  • PRBEN
  • Mass transfer coefficient Ω
  • Suspended sediment concentration
  • Active sediment zone depth
  • Water depth
  • Koc
## Model sensitivity with VVWM

<table>
<thead>
<tr>
<th>Factor</th>
<th>Base</th>
<th>Value 1</th>
<th>Value 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>PRBEN</td>
<td>0.5</td>
<td>0.25</td>
<td>0.75</td>
</tr>
<tr>
<td>Mass transfer coefficient Ω</td>
<td>$1 \times 10^{-8} \text{ m/s}$</td>
<td>$1 \times 10^{-7} \text{ m/s}$</td>
<td>$1 \times 10^{-9} \text{ m/s}$</td>
</tr>
<tr>
<td>Suspended sediment concentration</td>
<td>30 ppm</td>
<td>10 ppm</td>
<td>60 ppm</td>
</tr>
<tr>
<td>Active sediment zone</td>
<td>5 cm</td>
<td>20 cm</td>
<td></td>
</tr>
<tr>
<td>Water depth</td>
<td>2 m</td>
<td>15 cm</td>
<td></td>
</tr>
<tr>
<td>Koc</td>
<td>500 cc/g</td>
<td>5000 cc/g</td>
<td></td>
</tr>
</tbody>
</table>
Results

Who among you is staring at their phone?
PRBEN

Aqueous Concentration (µg/L)

Date

BaseW_PRBEN=0.5  W_PRBEN=.25  
W_PRBEN=.75  BasePW_PRBEN=.5  
PW_PRBEN=.25  PW_PRBEN=.75
Suspended sediment concentration

Suspended Sediment Comparison

Aqueous Concentration (µg/L)

Date

Jun  Jul  Aug  Sep  Oct  Nov  Dec  Jan

- BaseW_SS=30
- W_SS=10
- W_SS=60
- BasePW_SS=30
- PW_SS=10
- PW_SS=60
Water depth comparison

Water Depth Comparison

Aqueous Concentration (µg/L)

Date

Jun  Jul  Aug  Sep  Oct  Nov  Dec  Jan

15 cm

2 m

- BaseW_Depth=2m
- W_Depth=0.15m
- BasePW_Depth=2m
- PW_Depth=0.15m
Sediment depth comparison

![Graph showing sediment depth comparison]

- BaseW_Sed=5cm
- W_Sed=20cm
- BasePW_Sed=5cm
- PW_Sed=20cm
Mass transfer coefficient comparison

Mass Transfer Coefficient Comparison

Aqueous Concentration (μg/L)

Date

Jun Jul Aug Sep Oct Nov Dec Jan

BaseW_1e-8 W_1e-7 W_1e-9
BasePW_1e-8 PW_1e-7 PW_1e-9

1E-7 1E-8 1E-9
Koc comparison

Koc VVWM Comparison

Koc PRZM-VVWM Comparison

Aqueous Concentration (μg/L)

Date

Jun Jul Aug Sep Oct Nov Dec Jan

BaseW_Koc=500ml/g
W_Koc=5000ml/g
BasePW_Koc=500ml/g
PW_Koc=5000ml/g
## Equilibrium conditions

<table>
<thead>
<tr>
<th>Run</th>
<th>EOY concentration in pore water (µg/l)</th>
<th>DAT equilibrium &lt;1%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base</td>
<td>20.05</td>
<td>175</td>
</tr>
<tr>
<td>SS=10 mg/L</td>
<td>20.06</td>
<td>161</td>
</tr>
<tr>
<td>SS=60 mg/L</td>
<td>20.05</td>
<td>161</td>
</tr>
<tr>
<td>Sediment Depth=20 cm</td>
<td>8.64</td>
<td>328</td>
</tr>
<tr>
<td>PRBEN=0.25</td>
<td>20.04</td>
<td>166</td>
</tr>
<tr>
<td>PRBEN=0.75</td>
<td>20.07</td>
<td>156</td>
</tr>
<tr>
<td>Water Depth=15 cm</td>
<td>43.66</td>
<td>43</td>
</tr>
<tr>
<td>MTC =1e-7</td>
<td>20.11</td>
<td>24</td>
</tr>
<tr>
<td>MTC =1e-9</td>
<td>10.94</td>
<td>zzzzz</td>
</tr>
<tr>
<td>KOC = 5000 ml/g</td>
<td>4.41</td>
<td>56</td>
</tr>
<tr>
<td>PRZM KOC also =5000 ml/g</td>
<td>0.11</td>
<td>52</td>
</tr>
</tbody>
</table>
Conclusions & recommendations (1)

- The most sensitive variables with respect to equilibrium concentration and time to equilibria were Koc, water depth, depth of benthic zone, and MTC.
  - "Sensitive" depends on endpoint (e.g., acute, chronic)

- MTC as total water-sediment process needs further investigation
  - Can vary significantly - probably less in a "pond" and more in a "reservoir". What about wetlands?
  - Do we have empirical data relevant to what the regulatory scenario represents?
Conclusions & recommendations (2)

• Depth of “active sediment zone” needs to be considered in context to what it is being used for
  • Solely to establish a pore-water exchange zone?
  • Exposure in biologically relevant zone?
  • Calibrate model to a sediment core collected in the field?

• Next: comparison of predictions against field data
References

Thank You

Welcome your participation on this topic in a session at a future ACS or IUPAC meeting
## Model comparison matrix

<table>
<thead>
<tr>
<th>Model Acronym</th>
<th>EXAMS</th>
<th>VVWM</th>
<th>TOXWA</th>
<th>AGRO-2014</th>
<th>RIVWQ</th>
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</thead>
<tbody>
<tr>
<td><strong>Hydrodynamic / sediment processes</strong></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Spatial</td>
<td>3D</td>
<td>No</td>
<td>1D</td>
<td>No</td>
<td>1D, tributaries</td>
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<tr>
<td>Variable volume</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Variable flow</td>
<td>Manual</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Unsteady flow</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Tidal boundary conditions</td>
<td>Indirectly</td>
<td>No</td>
<td>Not sure</td>
<td>No</td>
<td>Indirectly</td>
</tr>
<tr>
<td>Suspended sediment concentration</td>
<td>Fixed</td>
<td>Fixed</td>
<td>Fixed</td>
<td>Dynamic</td>
<td>Both</td>
</tr>
<tr>
<td>Sediment settling</td>
<td>PRBEN</td>
<td>PRBEN</td>
<td>No</td>
<td>Cool</td>
<td>Yes</td>
</tr>
<tr>
<td>Sediment resuspension</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Bed sediment scour</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td><strong>Chemical Processes</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Degradation pathways</td>
<td>Individual</td>
<td>Individual</td>
<td>Bulk</td>
<td>Bulk</td>
<td>Hybrid</td>
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<td>Transformation products</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Partitioning in water column</td>
<td>SS and biota</td>
<td>SS and biota</td>
<td>SS and biota</td>
<td>SS</td>
<td>SS</td>
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<tr>
<td>Water-sediment transfer</td>
<td>Single MTC</td>
<td>Single MTC</td>
<td>Multiple</td>
<td>Multiple</td>
<td>Multiple</td>
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<tr>
<td>Burial</td>
<td>No</td>
<td>Optional</td>
<td>No</td>
<td>Dynamic</td>
<td>Constant</td>
</tr>
</tbody>
</table>
Foundation - partitioning and effective diffusion

\[ K_d = \frac{C_s}{C_w} \]

\[ M_{difus} = K_{difus} \times SA \times \left( \frac{F_{DS} \times C_s}{\phi} - F_{DW} \times C_w \right) \times dt \]

\[ F_{DW} = \frac{1}{1 + K_d \times C_{SS}} \]

\[ F_{DS} = \frac{\phi}{\phi + (K_d \times \rho_b)} \]

Kd = Water-sediment partition coefficient (L/kg)
Cs = Sorbed concentration (mg/kg)
Cw = Dissolved concentration (mg/L)
M_{difus} = Mass transfer between water and sediment
K_{difus} = Diffusion coefficient
SA = Surface area of water-sediment interface
C_{SS} = Suspended sediment concentration
F_{DS} = Dissolved fraction of chemical in sediment pore water
F_{DW} = Dissolved fraction of chemical in water column
\( \phi \) = Sediment porosity
\( \rho_b \) = Sediment bulk density
EPA’s tiered approach to risk assessment

Source: USEPA 2000